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Determination of Metaldehyde in Workroom Air

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Metaldehyde, is the tetramer of acetaldehyde. In acidic media, it readily depolymerizes to the very volatile monomer. Other than as a non-smoky, solid fuel, metaldehyde is commonly and globally used as a molluscicide. Generally, it is formulated as a 2 to 10% slug bait on a protein-rich milling offal, such as bran.

It is a moderately toxic substance (LD_{50} for dogs is 600–1000 mg/kg) (MARTIN & WORTHING 1974). However, it is irritating to skin and mucous membranes and can cause kidney and liver damage (SAX 1975). No Threshold limiting value (TLV) has yet been established for metaldehyde in the U.S.A. (A.C.G.I.H. 1979) or Italy. In the U.S.S.R. a tolerance limit recommended for the concentration of metaldehyde in air in work areas is 0.2 mg/m^3; it is based on toxicological inhalation studies (DOBRYANSKII 1974). In our pesticide formulating factory, a TLV of 0.5 mg/m^3 has been provisionally established. Therefore, a suitable analytical procedure was needed to monitor the ambient air in workrooms during the formulation of the slug-killing baits. This research was part of a more complete programme of analysis designed to monitor all the pesticides manufactured in our factory (MAINI & COLLINA 1979; COLLINA & MAINI 1979).

An "on-line" search for a bibliographic review of the analytical methods of metaldehyde in trace amounts was made. Metaldehyde residues were determined with spectrophotometry by GIANG & SMITH (1956) and KIMURA & MILLER (1964), with thin-layer chromatography by MAYS et al. (1968), and with GLC by SELIM & SEIBER (1973); all determinations were made after suitable extraction and cleanup procedures. The method of SELIM & SEIBER (1973) was previously used by us to analyse for metaldehyde residues in carrots and soil (MAINI 1974) and, more recently, by IWATA et al. (1982) for residues in citrus. For the monitoring of the metaldehyde dusts in workroom air, we adopted this method with some minor changes. Moreover, we developed a new and very simple method based on the

"head space" gas chromatography (HSGC) of the derived acetaldehyde and using the FID detector instead of the nitrogen-phosphorous specific detector (TSD) used in the first method.

MATERIALS AND METHODS

Workroom air sampling: The collection apparatus consists of a pre-weighed, microporous, filtering membrane (Gelman, Metricel DM-800, 0.8 µm porosity, 47 mm) held in its proper dust collector (Gelman Cod. n. 19.001220), connected by a rubber tubing to a Gelman EC-3000 apparatus (Gelman Instruments Spa., Opera (Milan), Italy). The latter is equipped with aspiration pump; timer; flow-, temperature-, and gas-meters. The air flow rate is about 20 L/min during a 4 h minimum collecting period.

Analysis: After weighing the filtering membrane to determine the total dusts present in the air, in mg/m^3, the analysis of the metaldehyde present in the very small amount of dust is carried out with one of the following procedures:

A) Dinitrophenylhydrazone (DNPH) of the acetaldehyde and TSD - GLC determination.

The SELIM & SEIBER (1973) procedure is followed in a simplified manner, because here it is not necessary to use cleanup steps. All the reagents (2,4-dinitrophenylhydrazine, 2,4-dinitrophenyl-hydrazine reagent (DNPH-reagent), and the 2,4-dinitrophenyl-hydrazone of acetaldehyde (DNPH-acetaldehyde)) are prepared as stated in the original paper. Benzene is washed with DNPH-reagent, according to IWATA et. al. (1982), to eliminate traces of acetone.

After weighing, the filtering membrane is carefully rolled up with forceps and introduced into a 15-mL screw-cap test tube; 5 mL of DNPH-reagent are added, and the test tube is immediately and tightly capped. After shaking in a Vortex-mixer, it is kept at room temperature, with periodical shaking. After 30 min, 5 mL of benzene are added, and the tube is shaken for 4-5 min. After separation of the layers, 5 µL of the benzene layer are injected in the gas chromatograph (Varian 3700, equipped with TSD detector), operating with a 170 x 0.3 cm i.d. silanized glass column packed with 1.5% OV-17 + 1.5% OV-210 on Gas-Chrom Q, 100-120 mesh, and the following temperatures: 240, 230, and 250°C, respectively, for injector, column oven, and detector. The gas flows are 30, 4.75, and 175 mL/min, respectively for

nitrogen carrier, hydrogen, and air. The quantitative determination is by means of a calibration graph, previously prepared injecting ethyl acetate solutions of DNPH-acetaldehyde standard, ranging 0.1-150 µg. Otherwise, a direct comparison of the sample peak with a DNPH-acetaldehyde standard solution can be done. Results are given in mg metaldehyde/m^3 air (stoichiometric ratio of metaldehyde/DNPH-acetaldehyde is 1:5.09). The precision of the method was controlled with known amounts of metaldehyde (in 1% mixture with talc; see procedure B): for amounts lower than 10 ng the deviation was ± 5.7%.

B) Head space gas chromatography (HS-GC) of acetaldehyde derived from metaldehyde.

As in the previous method, the filtering membrane is thoroughly rolled up and carefully introduced into a 40-mL screw-cap vial with Teflon-faced, silicone septum, as recommended by EPA for collecting and storage of water samples (Supelco Inc., Cat. no. 2-3285). 10 mL of abt. 20 N H_2SO_4 are added, and the vial is immediately and tightly capped and well shaken; it is then immersed in a 75°C water bath, placed as close as possible to the gas chromatograph, and kept there for at least 1 h. By means of a gas-tight, pre-heated (60°C) syringe (Hamilton, Cat. no. 1002 LTN), 1500 µL of the air from the vial (head space) are taken and injected in the gas chromatograph (Varian Aerograph 1440 B, equipped with FID). The whole operation has to be carried out as quickly as possible, to avoid cooling. The GC operating conditions are: 90 x 0.3 cm i.d. glass column packed with Porapak T; temperatures: 150, 100, and 220°C, respectively, for the injector, the column oven, and the detector; gas flows: 30, 30, and 300 mL/min, respectively, for carrier, hydrogen, and air. A typical chromatogram is shown in Figure 1.

Similar columns were used by others for acetaldehyde analysis. For example, DUMAS (1980) utilized both the Porapak N and the Chromosorb Century Series (101 and 107) for acetaldehyde in air, after trapping and desorption on Tenax GC.

The quantitative determination is made with a calibration graph: The standards are prepared by carefully mixing analytical grade metaldehyde with talc in the ratio 1:100 (w/w). Different amounts of the mixture, ranging 10-300 µg of metaldehyde are accurately weighed into the EPA vials; then the described procedure is carried out for each of them. Resulting graph is shown in Figure 2.

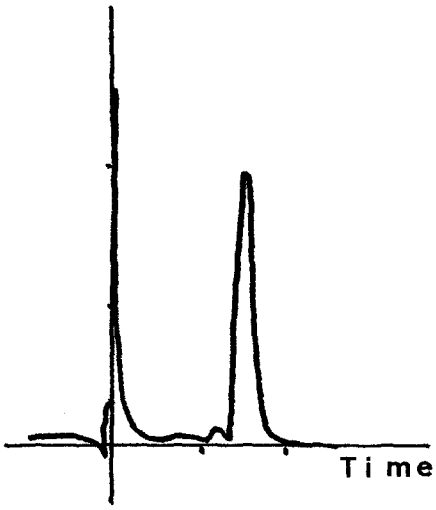

Fig. 1 - Head space gas chromatography of acetaldehyde derived from 45 µg of metaldehyde. Column: Porapak T.

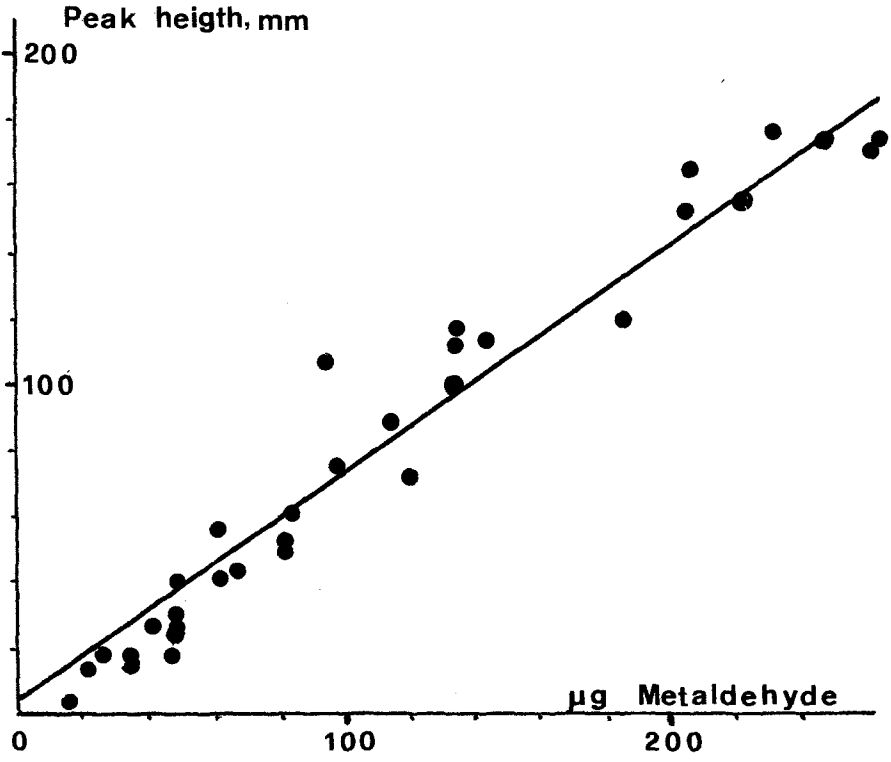

Fig. 2 - Calibration graph for metaldehyde, by HSGC of derived acetaldehyde.

DISCUSSION

Both the procedures developed for metaldehyde in trace amounts in the dust of workrooms' air are reliable. However, a comparison between the two methods could be made in terms of simplicity and sensitivity. The new HS technique for acetaldehyde derived from metaldehyde dust is extremely simple and quick; it does not require rare or very purified reagents; moreover, the FID detector is widely used in all laboratories. Perhaps the use of an automatic and thermostated sampler/injector should enchance the precision of the method. It is probable, indeed, that the imprecision of the measurements in the preparation of the calibration curve (Figure 2) are due to the imperfect reproducible thermal conditions during the manual taking of the aliquots from the vial and the subsequent unreproducibility of the syringe temperature during injection.

However, the calibration graph, built with the regression equation, gives quite a good correlation factor ($R = 0.958$).

The sensitivity of the HSGC method, however, is poor and in practice it can not be used when the collected total dust in the membrane weighs less than 1 mg (generally metaldehyde is $\leq 1\%$ in total dust).

On the contrary, the DNPH-acetaldehyde method is very sensitive and allows the determination of 0.1 μg of metaldehyde, but it needs the preparation of special and particularly pure reagents and the use of the not very common phosphorous-nitrogen specific detector.

In conclusion, the choice of the methods depends mainly upon the required sensitivity; otherwise the head space technique (HSGC) should be the most suitable, mainly if a thermostated autosampler could be available. We think the HSGC method would be better applied in metaldehyde synthesis plants.

REFERENCES

A.C.G.I.H., (American Conference of Governmental Industrial Hygienists), Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment for 1979.

COLLINA, A. & P. MAINI: Bull. Environ. Contam. Toxicol. 22, 400 (1979).

DOBRYANSKII, V.M.: Gig. Tr. Prof. Zabol. 2, 55 (1974) reported

in Chem. Abstr. 81 (17), 100385 (1974).
DUMAS, T.: J. Chromatog. 200, 206 (1980).
GIANG, P.A. & P.F. SMITH: J. Agric. Food Chem. 4, 623 (1956).
IWATA, Y., G.E. CARMAN, T.M. DINOFF, & F.A. GUNTHER: J. Agric. Food Chem. 30, 606 (1982).
KIMURA, Y. & V.L. MILLER: J. Agric. Food Chem. 12, 249 (1964).
MAINI, P.: SIAPA/CER, Galliera, Italy. Report N° 3/74 Unpublished (1974).
MAINI, P. & A. COLLINA: Paper presented at the 2nd Congress of A.I.D.I.I. (Italian Assoc. of Industr. Hygienists), Bolzano, June, 1979. Published in: "Giornale Igienisti Ind.," Suppl. 4, 50-65 (1980).
MAYS, D.L., G.S. BORN, J.E. CHRISTIAN: Bull. Environ. Contam. Toxicol. 3, 366 (1968).
MARTIN, H. & G. R. WORTHING: "Pesticide Manual", 4th Ed., B.C.P.C., 1974.
SAX, I.N.: "Dangerous Properties of Industrial Materials", 4th Ed., Van Nostrand Reinhold Co., New York, 1975.
SELIM, S. & J.N. SEIBER: J. Agric. Food Chem. 21, 430 (1973).

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